OAK RIDGE
NATIONAL LABORATORY
MANAGED BY UT-BATTELLE
FOR THE DEPARTMENT OF ENERGY

CRADA No. ORNL02-0638

with Sasol North America Inc.

# "Atomistic Processes of Catalyst Degradation"

# Final Report

UT-BATTELLE
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**1. Abstract**

The purpose of this cooperative research and development agreement (CRADA) between Sasol North America, Inc. and the Oak Ridge National Laboratory (ORNL) was to improve the stability of alumina-based industrial catalysts through the combination of aberration-corrected scanning transmission electron microscopy (STEM) at ORNL and innovative sample preparation techniques at Sasol. Outstanding progress has been made in task 1, "Atomistic processes of La stabilization". STEM investigations provided structural information with single-atom precision, showing the lattice location of La dopant atoms, thus enabling first-principles calculations of binding energies, which were performed in collaboration with Vanderbilt University.

The stabilization mechanism turns out to be entirely due to a particularly strong binding energy of the La atom to the γ-alumina surface. The large size of the La atom precludes incorporation of La into the bulk alumina and also strains the surface, thus preventing any clustering of La atoms. Thus highly disperse distribution is achieved and confirmed by STEM images. La also affects relative stability of the exposed surfaces of γ-alumina, making the 100 surface more stable for the doped case, unlike the 110 surface for pure γ-alumina. From the first-principles calculations, we can estimate the increase in transition temperature for the 3% loading of La used commercially, and it is in excellent agreement with experiment.

This task was further pursued aiming to generate useable recommendations for the optimization of the preparation techniques for La-doped aluminas. The effort was primarily concentrated on the connection between the boehmite - $\gamma$-$Al_2O_3$ phase transition (*i.e.* catalyst preparation) and the resulting dispersion of La on the $\gamma$-$Al_2O_3$ surface. It was determined that the La distribution on boehmite was non-uniform and different from that on the $\gamma$-$Al_2O_3$ and thus apparently La dispersion happened simultaneously with the boehmite - $\gamma$-$Al_2O_3$ phase transition. It was further discovered that oxygen, moisture, or the combination thereof are crucial in achieving optimal La dispersion and desired thermal stabilization.

Finally, several samples were studied as a part of task 2, "Study of organophilic modification of aluminas", and determined that the high vacuum environment of our STEM removes all the organic ligands from the alumina surface and thus needs to be studied in a different instrument able to handle pressures closer to ambient.

**2. Statement of objectives.**

The purpose of the CRADA was to improve the stability of alumina-based industrial catalysts, using the sub-angstrom microscopy capabilities at Oak Ridge to reveal changes in the distribution, shape, size and chemical state of the metal catalyst, dopant and impurity species.

**3. Benefit to funding DOE office's mission**

The catalysts represent the ideal test specimens for the development of aberration-corrected scanning transmission electron microscopy, providing a test both of the resolution and also of the sensitivity to individual atoms. These specimens provided one of the first direct comparisons between uncorrected and corrected imaging, showing the enormous improvement of aberration correction. The study demonstrated the great potential of this technique for understanding catalysis at the atomic level.

**4. Technical Discussion of Work**

At high temperatures (~1100 °C), $\gamma$-$Al_2O_3$ undergoes a transformation to the non-porous, thermodynamically stable $\alpha$-$Al_2O_3$ phase (corundum), which shows no catalytic activity. Incorporation of dopants such as La has been found empirically to raise the transformation temperature to ~1250 °C, enabling a critical list of applications. Optimization of the process, however, has not been achieved. In the industrial process, 3-5 wt% La is needed to achieve desirable results. Laboratory experiments, on the other hand, have demonstrated comparable stabilization with only roughly 0.3%, which signals a significant potential economic benefit because La is quite expensive. However, knowledge of the mechanism by which stabilization is achieved is lacking for both the industrial and the laboratory processes. On the basis of very limited information, there have been conflicting suggestions that La forms $LaAlO_3$ or $La_2O_3$ monolayers on $\gamma$-$Al_2O_3$ surfaces or it is incorporated in the bulk. There have been no suggestions about the atomic-scale processes that actually delay the onset of the transformation process. Thus, optimization of the thermal stability of $\gamma$-$Al_2O_3$ –based catalysts, which is an important step in the pursuit of the "catalyst-by-design" objective remains an open issue.

Combined experimental and theoretical investigations have been performed that include direct atomic-resolution Z-contrast imaging of La-doped $\gamma$-$Al_2O_3$ and first-principles density-functional total-energy calculations. These yield complementary information that amounts to a single overriding conclusion: La atoms eschew the bulk and adsorb strongly on $\gamma$-$Al_2O_3$ surfaces as ***single atoms*** without any clustering. We infer that La atoms stabilize the $\gamma$-$Al_2O_3$ phase by inhibiting sintering, which would result in locking La atoms in a bulk environment. A complementary theoretical result reveals a second role for La: adsorption of La on $\alpha$-$Al_2O_3$ surfaces occurs with a much smaller binding energy (~4 eV versus ~8 eV). The increase in the enthalpy difference of the two phases pushes the transformation temperature higher.

The experiments and theory provide additional information that corroborates the main conclusion and elucidates the mechanism by which the phase transition is impeded. In particular, by varying the defocus of the electron beam, Z-contrast microscopy shows a definite correlation of the imaged La atoms with the top and bottom surfaces of the sample. Theory and atomic-resolution imaging agree on the preferred surface configuration of La atoms and theory establishes that adsorbed La atoms induce substantial local reconstruction, which is responsible for the strong binding. In turn, strong binding and local reconstruction lead to a large energy barrier for La surface diffusion (~4-5 eV), suggesting that stabilization of $\gamma$-$Al_2O_3$ is likely up to temperatures when La diffusion becomes feasible. Thus, contrary to earlier suggestions, the formation of a surface La-oxide layer does not occur at low enough temperatures to be responsible for the inhibition of sintering.

Z-contrast STEM observations were made with VG Microscopes HB603U operated at 300kV and equipped with Nion® aberration corrector to give probe size of 0.7-0.8 Å and superior signal-to-noise ratio. La-doped $\gamma$-$Al_2O_3$ sample annealed at 1000°C was used for the investigation because of higher crystallinity compared to untreated samples. Surprisingly, unlike the undoped case, there was no apparent preferential exposure of the [110] surface. Instead, the [100] surface was encountered often. Fig. 1(a) shows a Z-contrast image of a flake of La-doped $\gamma$-$Al_2O_3$ in the [100] orientation. A square arrangement of Al-O columns is clearly resolved. In this imaging mode, the intensity

contributed by an atom is roughly proportional to $Z^2$, where Z is the atomic number. allowing single La atoms to be visible in the form of brighter spots on the background of thicker but considerably lighter $\gamma$-$Al_2O_3$ support. Most of the La atoms are located directly over Al-O columns (site A in Fig. 1), but a small fraction also occupies a position shifted from the Al-O column (site B in Fig. 1). Note that, in this second configuration, the La atom appears dimmer, because its intensity is no longer superimposed on that of the Al-O column; this effect is also evident in simulated images (Fig. 1(b)). The images reveal clearly that *there is no apparent correlation in the distribution of dopant atoms.* The presence of La was also confirmed by electron energy loss spectroscopy (EELS).

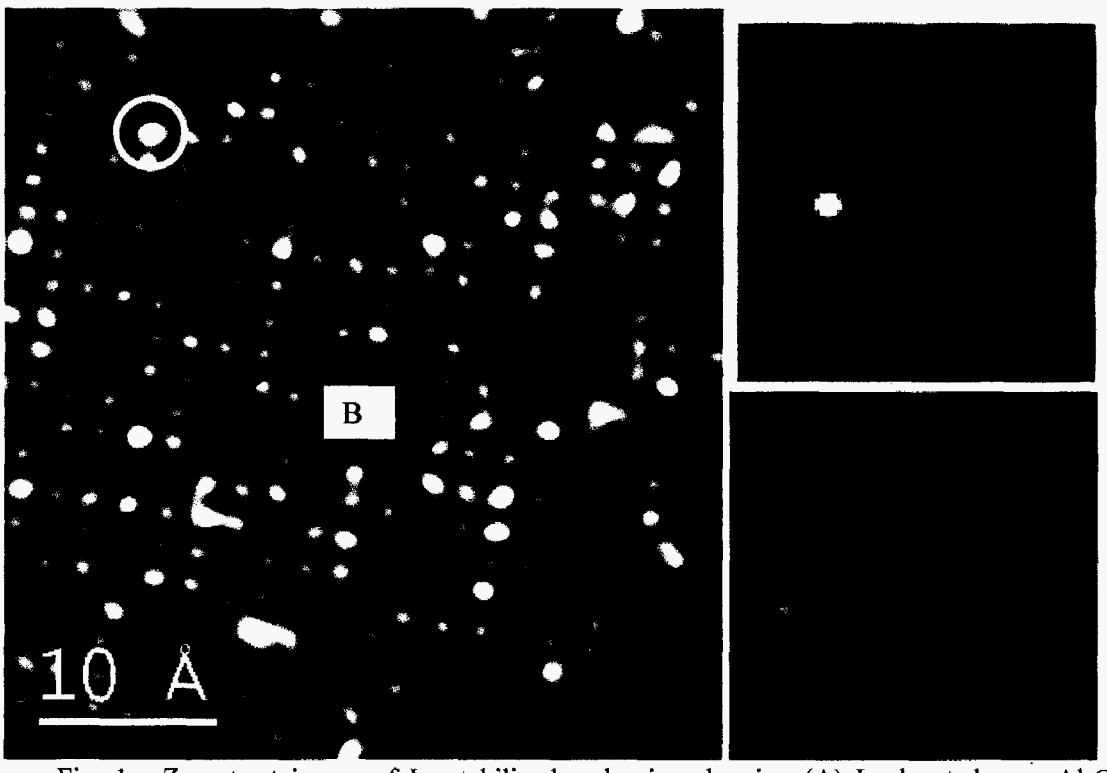



Fig. 1: Z-contrast image of La-stabilized $\gamma$-alumina showing (A) La located over Al-O columns of the alumina, and (B) interstitial locations, with corresponding image simulations.

While Z-contrast image is effectively a 2D projection of the 3D object, the higher convergence angle of the aberration-corrected STEM probe offers a possibility of depth sensitivity utilizing the decreased depth of focus. Under these conditions, the intensity of an image of a point object (such as single atom) significantly diminishes when it is only nanometers away from the perfect focus. We find that for La-doped $\gamma$-$Al_2O_3$ flakes in the absence of any lattice contrast from the substrate (i.e. when it is tilted far off crystallographic axes) two different focus conditions can be identified, which can be attributed to La atoms located on the top and bottom surface of the flake, respectively. Fig. 2 shows an example of such through-focal series of Z-contrast STEM images. While individual atoms cannot be unambiguously traced from frame to frame due to beam-induced movement, images at defocus values of 0 and -8 nm appear sharper than the rest of the sequence, suggesting that the thickness of the examined flake is close to 8 nm. Note that after going past the bottom surface atoms "fade" faster, reflecting widening of

the probe after passing through the substrate. This unique experiment demonstrates a depth-sensing capability of the STEM and corroborates the conclusion that La atoms prefer surface positions as opposed to bulk. Exploration of the full potential of depth profiling by the STEM is now underway.

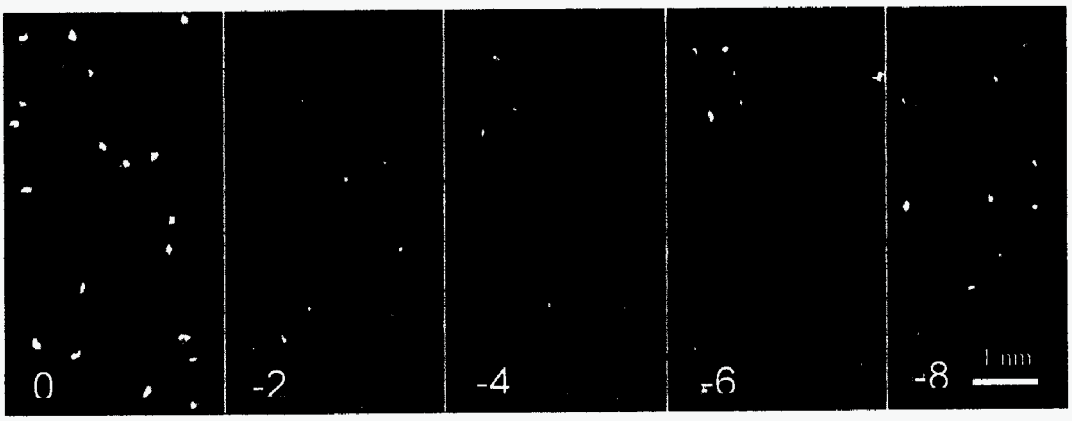
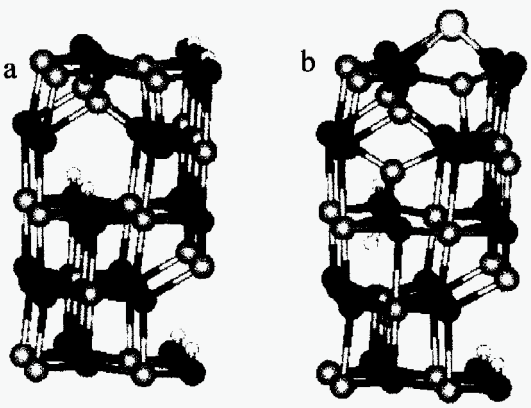



Fig. 2. Images of single atoms on the top and bottom surfaces of γ-alumina as the beam focus is varied. Atoms on top show clearest in focus and those on the bottom are seen clearly at –8 nm defocus.

The first-principles calculations were performed within density functional theory, using the pseudopotential method and a plane wave basis set.. In the absence of La, the (100) surface (Fig. 3a) shows only minor relaxation effects; all the surface aluminum atoms are five-coordinated and the surface oxygen atoms are either three- or four-coordinated. The cation vacancies are located between the first and second oxygen subsurface layer. However, when a La atom is introduced, a significant relaxation of the structure occurs. One of the five-coordinated Al atoms (adjacent to La) is displaced from the surface into the subsurface tetrahedral vacancy site (Fig. 3b). The La atom occupies the resultant surface fourfold hollow site, which is close to the initial location of the Al atom in planar coordinates but located ~1.2 Å above it, making La-O bond lengths 2.3-2.5 Å. This configuration, obtained independently by total-energy minimization, is precisely the same as the "site A" on the micrograph in Fig. 1(a). Calculations aimed at revealing the structure of the observed B site found that it corresponds to a La atom with one of the four neighboring surface O atoms missing. The asymmetry forces the La atom off the Al-O column, as observed. Its formation is clearly the result of the presence of surface O vacancies.

Fig. 3: Relaxed atomic configurations of (a) a clean (100) γ-alumina surface, (b) a La-doped γ-alumina surface.



Additional calculations exploring the incorporation of La atoms in bulk $\gamma$-$Al_2O_3$ found that a La atom, when initially placed at a vacancy, interstitial, or substitutional site in the second or third subsurface layer, would relax up to the surface. When a La atom is initially located in a deeper layer (the $8^{th}$ or $9^{th}$ layer of the supercell for the (100) surface, and the $5^{th}$ or $6^{th}$ layer for the (110C) surface), which is equivalent to the bulk, the total energy of the system is significantly higher than that of the configuration with La on the surface (models with La in different bulk sites were examined). The preference for surface site over the bulk arises primarily from the large difference in ionic size between $La^{+3}$ (1.03 Å) and $Al^{+3}$ (0.54 Å). The theoretical result corroborates the through-focus imaging analysis of Fig. 2. The marked preference for surface sites versus the bulk is an important factor in the inhibition of sintering. Progress of the sintering process would inevitably trap some of the surface La atoms in the bulk, thus forcing the system into highly strained and energetically unfavorable configuration. The resulting inhibition effect helps retain large surface area of $\gamma$-$Al_2O_3$ at higher temperatures.

The binding energy of La to the (100) surface is very high (8.6 eV), due partly to the removal of the surface Al atom into the subsurface, which enhances the attractive interaction between La and the surface O atoms and reduces the otherwise strong repulsion between La and the Al atom. The strong binding also causes large migration energies (4-5 eV) for typical paths connecting equivalent configurations. Similar calculations for the (110C) surface, which is exposed preferentially in the *undoped* $\gamma$-$Al_2O_3$,[25,26] also resulted in high values of the binding energy (7.5 eV). In this case, however, La atoms occupy existing surface hollow sites, which are created on the undoped surface[26,27] by displacement of three-coordinated surface Al atoms into the empty octahedral sites in the first subsurface layer. This difference in the two binding energies is likely responsible for the observed occurrence of (100) surfaces only after annealing in the presence of La dopant (Fig. 4).

When the same computational procedure is carried out for $\alpha$-$Al_2O_3$ (0001) surface, much lower binding energy (4.3 eV) for La atoms is obtained. This difference means that doping causes an increase in the enthalpy difference $\Delta H$ between the two phases. If we assume that doping leaves the entropy difference $\Delta S$ between the two phases roughly unchanged, the thermodynamic relation

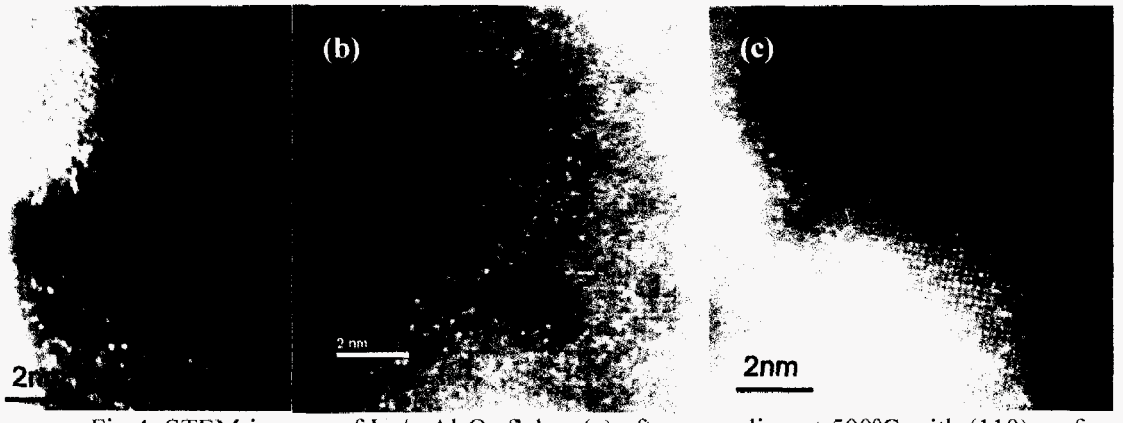



Fig.4. STEM images of La/$\gamma$-$Al_2O_3$ flakes (a) after annealing at 500°C with (110) surface preferentially exposed and (b), (c) after annealing at 1000°C with (100) surface preferentially exposed.

$\Delta G = \Delta H - T\Delta S$,

suggests that $\Delta G = 0$, which signals the possible onset of a transformation, requires higher temperatures. Experiments have established a relationship between temperature and the surface-to-mass ratio, which changes because of sintering, and measured $\Delta H$ and $\Delta S$ for undoped phases at the transformation temperature of 1100°C. If the role of La were simply to increase $\Delta H$ with no effect on the rate of sintering, we can use the experimental data and our theoretical value of doping-induced $\Delta H$ to predict a doping-induced increase of the transformation temperature. The result depends on the La concentration. For typical concentrations, x, y, z, we get transformation temperatures *X*, *Y*, *Z*. However, as noted earlier, La also inhibits sintering so that the reduction of the surface-to-mass ratio with increasing temperature is much slower when $\gamma$-$Al_2O_3$ is doped, meaning that the transformation temperature will be pushed even higher.

Stabilization of $\gamma$-$Al_2O_3$ by La is often suggested to be due to $LaAlO_3$ or $La_2O_3$ monolayers on the surface, and the debate about the formation of one phase over another is still ongoing. We explored the possibility of clustering of surface La atoms. When placed in the nearest interstitials above the (110C) surface of $\gamma$-$Al_2O_3$, two La atoms do not show any tendency to create any bond between them. Instead, *they move away from each other when the initial distance between them is less than 4 Å*, thus suggesting that there is no driving force for the formation of dopant clusters or monolayers, unlike previously proposed. This effect suggests that the sintering can be effectively inhibited by a very small amount of La dopant, provided that atomically dispersed distribution can be achieved by a given preparation method. The mechanism also suggests that excess La in the form of compounds may be unnecessary for stabilization.

The final stage of the project was aimed at developing concrete suggestions for the materials processing from our improved understanding, both structural and theoretical, of nanoscale dopant distribution and the mechanisms involved in delayed $\gamma$- to $\alpha$- phase transition of the La-modified alumina supports. To achieve optimal dopant distribution we need to consider in detail the behavior of La from the precursor to the final product.

The route commonly used in industry for preparation of the La-doped alumina involves impregnation of the boehmite (AlOOH) powders with the aqueous solution of a La compound and subsequent annealing at 500° C to convert boehmite into $\gamma$-$Al_2O_3$. Note that this is another phase transition that can also be affected by the addition of La. We have thus investigated La distribution on boehmite substrate prior to its conversion into $\gamma$-$Al_2O_3$.

Two representative STEM images are given in Fig.5. It appears that unlike the case of $\gamma$-$Al_2O_3$, La distribution on boehmite is non-uniform. Both isolated La atoms (Fig. 5(a)) and 1-2 nm La-containing particles (Fig. 5(b)) can be found, suggesting that La dispersion happens not immediately during impregnation but at a later stage of the process.

It was also interesting to determine if the change in preferential orientation mentioned earlier (see Fig. 4) occurs only after high temperature annealing or is present at lower temperatures as well to a lesser degree. To answer this question it was necessary to obtain a statistically valid estimate of the abundance of different exposed surfaces after different temperature treatments.

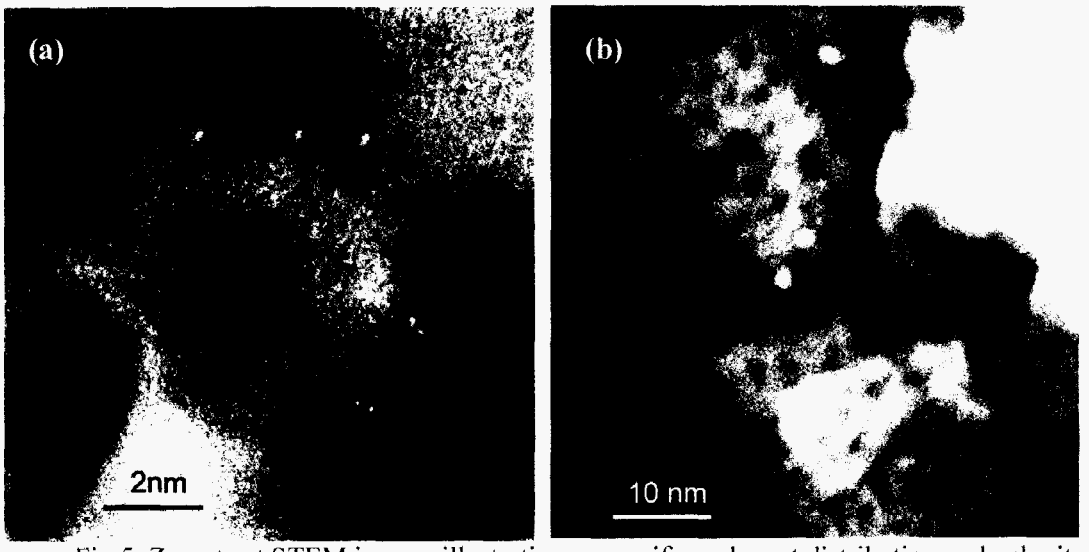



Fig.5. Z-contrast STEM images illustrating non-uniform dopant distribution on boehmite: (a) single La atoms; (b)nm-scale La particles

Sample preparation techniques utilized previously in the project, such as dispersion of the dry powder on carbon film, or immersion of holey carbon grids into the sol with subsequent drying, were found unsatisfactory because they resulted in the agglomeration of the particles and consequently problems in determining the orientation of any particular grain due to excessive overlap. An alternative sample preparation method was then tried. Boehmite powders were infused with La solution and dispersed on a molybdenum grid coated with holey carbon film. The grid was then freeze-dried to eliminate water while maintaining particle dispersion. The resulting grid was then heated at 500°C in inert atmosphere to avoid oxidation.

This process has allowed us to achieve the improved dispersion, as illustrated in Fig. 6. Instead of large spherical clumps of particles with randomly oriented overlapping

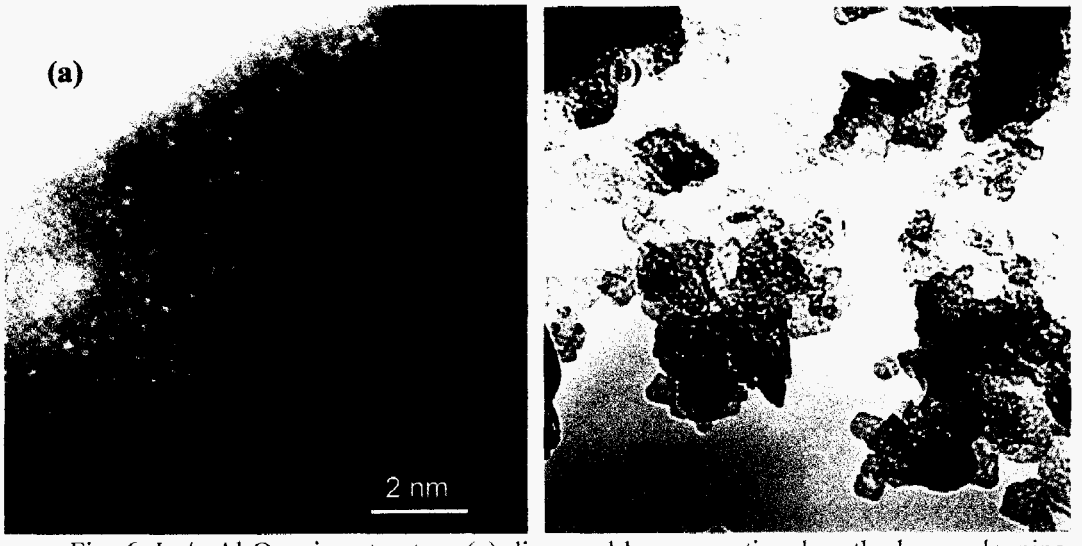



Fig. 6. La/γ-$Al_2O_3$ microstructure (a) dispersed by conventional methods: overlapping grains (HAADF STEM image) (b) dispersed as boehmite than freeze-dried: more isolated, similarly oriented grains (TEM image).

flakes protruding from the surface, the particles instead form largely flat lacelike structures where all flakes are similarly oriented and the overlap is much less significant (Fig. 6(b)).

Surprisingly, however, the Z-contrast STEM studies of the freeze-dried samples have revealed a very different La distribution compared to the samples previously studied (Fig. 7). La atoms appear to attach to the surface in the form of patches and not individual atoms. It thus became apparent that freeze-dried samples, while providing very good alumina flake dispersion, cannot be used to study La distribution in conventionally prepared La-doped alumina powders. Clearly, a stage crucial to La dispersion was missing from the freeze-dried sample preparation process, thus changing the chemical form of the surface La and making it susceptible to agglomeration. This change could either be the nitrogen atmosphere instead of air, or dry environment instead of wet.

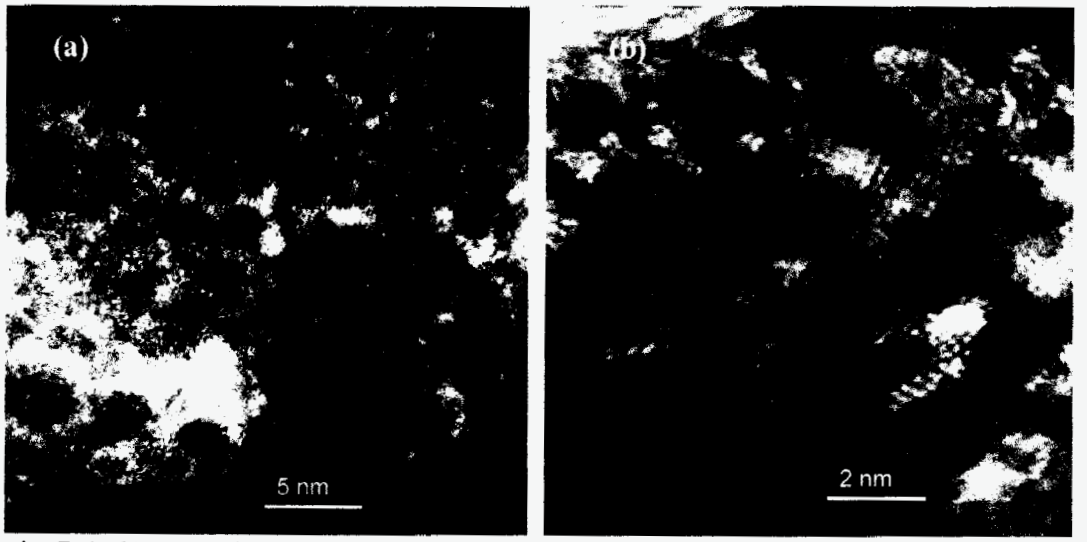



Fig. 7. (a, b) STEM images of the freeze-dried samples demonstrating clusters of La atoms. Distortions in (b) are due to sample charging.

We have also attempted to study aluminas modified with organophilic compounds however these samples proved to be unsuitable for STEM characterization because of high volatility in the vacuum environment of our microscope. The use of an environmental STEM appears to be necessary for this study and could provide substantial insights.

**5. Subject Inventions**

No protected intellectual property was generated in the course of this project.

**6. Commercialization Possibilities**

No commercialization possibilities are envisioned at this time.

**7. Plans for Future Collaboration**

An agreement exists to investigate a series of La-doped alumina samples with the purpose of determination whether humidity or oxygen environment (or both) is needed for the best dispersion of La on the substrate. Prospects of environmental microscopy of the organophilically modified aluminas, once it becomes available at ORNL, are also being discussed.

**8. Summary**

This project demonstrates the benefits that fundamental studies can bring to the field of catalysis. Even though the investigations were still a step away from generating concrete recommendations for the catalyst synthesis process, a wealth of useful information was generated that will be taken into account by the partner company in the future. The project has also served well to showcase the ORNL's aberration corrected scanning transmission electron microscopes; the benefits of aberration correction (such as single-atom sensitivity as well as the possibility of depth-resolved imaging) were most clearly demonstrated on these catalytic samples.